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CRYSTALLIZATION OF HIGH BULK DENSITY NITROGUANIDINE

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14. ABSTRACT Nitroguanidine (NQ) is an important high explosive widely used as a propellant. Conventionally, NQ is obtained as a long needle or rod shaped crystal that has a very low bulk density and cannot be used in propellant application. In this work, high bulk density NQ was obtained with a bulk density of 0.81 g/mL by controlled cooling of a supersaturated water solution of NQ containing methylcellulose and partially hydrolyzed polyvinyl alcohol (PVA). The dissolved NQ concentration in water solution containing methylcellulose and PVA was measured by following the absorption of infrared spectra, and the supersaturation level was calculated as the difference between the measured dissolved concentration and the solubility, also measured in the present work. Experiments were also conducted to obtain the kinetics of the crystallization. It appears from the experiments on kinetic studies that without the additives, the growth of the crystals in one direction is many times faster than other directions resulting in needle or rod shaped crystals, while the additives restrict the growth in that direction resulting in a more uniform growth in all directions.					
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INTRODUCTION

Nitroguanidine (NQ), a low sensitive high explosive, is widely used as a propellant. However, only high bulk density NQ (HBNQ) can be used as a propellant. Nitroguanidine is obtained conventionally in long rod or needle shaped crystals with a bulk density in the range of 200 to 300 g/L (ref. 1). The HBNQ is prepared from these rods or needles in a commutator with a hammer speed of 7500 rpm to reduce the particles to the desired size. The potential for explosion remains in this crushing operation. Moreover, the HBNQ produced by this method is also rod or needle shaped and therefore difficult to use in an explosive manufacturing processes such as extrusion or melt casting.

There are several patents that describe the formation of HBNQ by re-crystallization. For example, Thiel and Heinisch (ref. 2) described the formation of HBNQ by controlled cooling of a supersaturated solution of dimethylformamide, dimethylsulfoxide, etc. Henry and Cohen (ref. 3) obtained HBNQ by controlled cooling of a supersaturated NQ solution in water containing nitroguanyl hydrazone of benzaldehyde as an additive. Wagaman et al (ref. 4) obtained HBNQ from a supersaturated water solution containing methylcellulose and partially hydrolyzed polyvinyl alcohol (PVA). None of these works described the kinetics of change in supersaturation levels with time using seeds. By using crystals seeds, the final crystal sizes can be controlled. In this work, different re-crystallization methods were tried to obtain HBNQ crystals. By controlled cooling from a supersaturated water solution containing methylcellulose and partially hydrolyzed PVA, HBNQ crystals (bulk density of 0.81 g/mL) were obtained. This method of crystallization using seed crystals was used to obtain a desupersaturation rate with and without additives. It was found that the desupersaturation rate in water without any additives is much faster than the desupersaturation rate using methylcellulose and PVA. Without the additives, the growth of crystals in one direction appears to be much faster, resulting in needle or rod shaped crystals. Methylcellulose and PVA are probably restricting the growth in that direction resulting in more uniform growth in all directions giving bulkier crystals.

EXPERIMENTAL

Experiments were conducted in an automated apparatus manufactured by Mettler Toledo, model RC-1. The apparatus consists of a 1-L jacketed glass vessel with automatic controls for stirring speed and temperature. Some experiments were also conducted in vials and a spray dryer. The temperature in the RC-1 vessel could be controlled within 0.1°C range by circulating heating or cooling fluid through the jacket. Microscopic pictures of NQ crystals were obtained using an optical microscope after obtaining solid crystals, which were filtered and washed using acetone. For measuring dissolved NQ concentration in the RC-1, a Mettler Toledo infrared (IR) ReactIR-4000 was connected to the vessel. A diamond probe was used to obtain the IR spectra from the vessel liquid. Spectrum having wave numbers within the range of 650 to 4000 cm^{-1} could be collected using this equipment. The concentration of dissolved NQ was obtained by using the IR spectra data.

RESULTS AND DISCUSSION

Formation of High Bulk Density Nitroguanidine

Re-crystallization of Nitroguanidine by Controlled Cooling from a Solution in Ethylene Glycol

Nitroguanidine (8.013 g) was dissolved in 250 mL of ethylene glycol in the RC-1 crystallizer by heating the content to 90°C. Cooling of the crystallizer was started when all the NQ dissolved and the measured cooling rate was found to be approximately 2.5°C/min. The stirrer speed during the crystallization was 300 rpm. Crystals were found to form at around 25°C. When the temperature of the crystallizer reached 15°C, a small part was filtered through Whatman 41 filter paper, washed using acetone, and the crystals were analyzed with an optical microscope. Figure 1 shows a picture of the crystals obtained by this method. The crystals formed from this method were rod shaped.



Figure 1

Optical microscope picture (100X) of NQ crystals (100X) obtained from controlled cooling of saturated solution of NQ in ethylene glycol at 2.5°C/min NQ re-crystallization from supersaturated solution in water containing methylcellulose and partially hydrolyzed PVA

The HBNQ crystals were obtained by controlled cooling of a supersaturated solution of NQ in water containing methylcellulose and partially hydrolyzed PVA. The initial dissolved NQ concentration and rate of cooling were varied to see if these variables have any effects on the crystals shape. In the runs, the mixture was initially heated to a temperature where all the solutes dissolved in water and then the cooling was started.

Effects of Initial Dissolved Nitroguanidine Concentration

A decrease in initial dissolved NQ concentration resulted in a decrease in onset crystallization temperature. Figures 2 to 4 show the optical microscope pictures of the NQ crystals obtained with 4.4% (w/w), 3.7% (w/w), and 3.2% (w/w) initial dissolved NQ solutions, but with a fixed cooling rate of 2.5°C/min. In all these runs, amounts of methylcellulose and PVA were 11% by weight of the NQ amount. The stirrer speed was 200 rpm. The temperatures at which crystallization started were 70, 62, and 55°C, respectively, corresponding to the three initial dissolved concentrations of NQ.

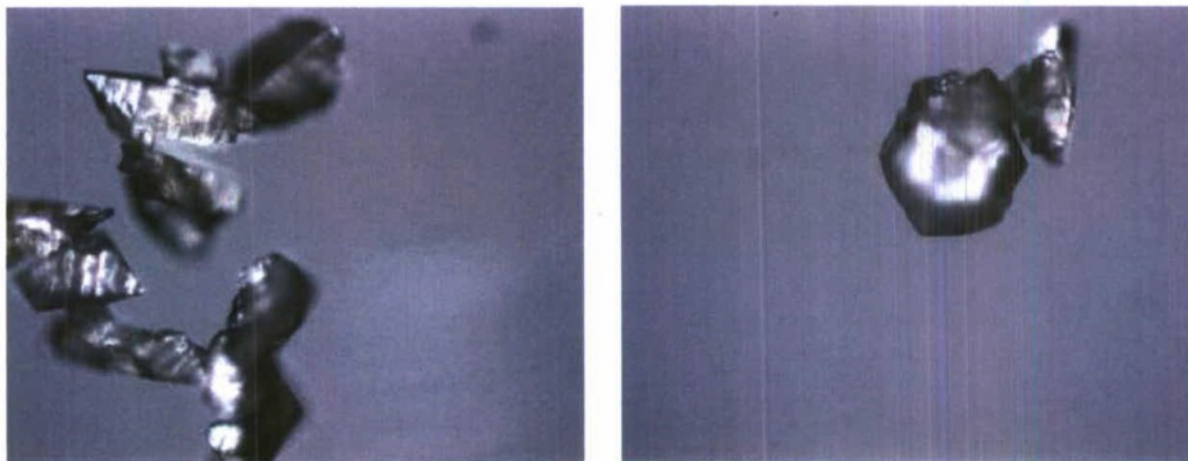


Figure 2

Optical microscope picture (100X) of NQ crystals obtained from controlled cooling at 2.5°C/min of supersaturated solution of NQ (initial NQ=4.4% w/w) in water containing methylcellulose and PVA



Figure 3

Optical microscope picture (100X) of NQ crystals obtained from controlled cooling at 2.5°C/min of supersaturated solution of NQ in water (initial NQ=3.7% w/w) containing methylcellulose and PVA



Figure 4

Optical microscope picture (100X) of NQ crystals obtained from controlled cooling of supersaturated solution of NQ in water (initial NQ=3.2% w/w) containing methylcellulose and PVA at 2.5°C/min

Effect of Cooling Rate

As mentioned, figure 3 shows the optical microscope picture of crystals obtained from controlled cooling of NQ solution with an initial concentration of 3.7%, and each of the methylcellulose and PVA amounts 11% of the NQ amount with a controlled cooling rate of 2.5°C/min. Using the same concentrations of NQ, methylcellulose, and PVA - another controlled cooling run was made using a cooling rate of ~4°C/min. Figure 5 shows the microscope picture of the crystals obtained.

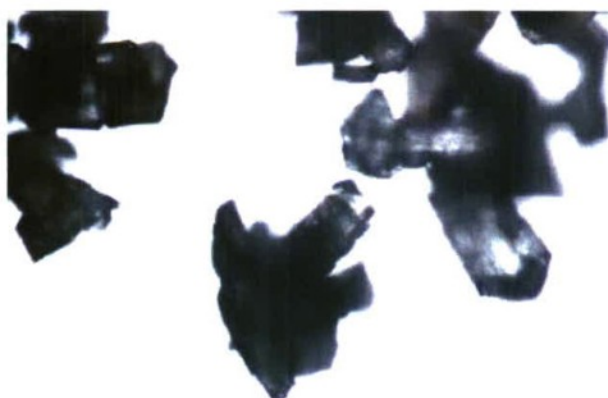


Figure 5

Optical microscope picture (100X) of NQ crystals obtained from controlled cooling of supersaturated solution of NQ in water (initial NQ = 3.7% w/w) containing methylcellulose and PVA at ~4°C/min

It appears from these pictures that the initial NQ concentration and cooling rates can be varied to some extent yielding HBNQ, and crystal shapes remain similar with variations of the parameters in these ranges.

Nitroguanidine Re-crystallization from Supersaturated Solution in N-methylpyrrolidine

Figure 6 shows the microscope picture of NQ crystals obtained from a 22% (w/w) of NQ solution in n-methylpyrrolidine (NMP) in a vial from 90 to 10°C in 5 min by immersing the vial in ice-cold water while stirring the mixture using a magnetic stirrer. The crystals were found to be needle shaped.



Figure 6

Optical microscope picture (100X) of NQ crystals obtained from cooling of 22% (w/w) solution of NQ in NMP

Antisolvent Crystallization of Nitroguanidine

A 22% (w/w) NQ solution in NMP was made by heating the mixture in a vial. Acetone, an antisolvent for NQ 1.5 times by volume of the solution at ambient temperature, was mixed with the solution. The mixture was further cooled by immersing the vial in ice-cold water while stirring the mixture using a magnetic stirrer. The crystals formed were also needle shaped as shown in figure 7.



Figure 7

Optical microscope picture (100X) of NQ crystals obtained from adding a 22% (w/w) solution of NQ in NMP to antisolvent acetone and then cooling the mixture

Nitroguanidine Crystallization by Spray Drying

A water solution containing NQ at room temperature was spray dried at 100°C and an optical microscope image was taken of the spray-dried crystals (fig. 8). Needle shaped crystals were found to form in the spray drying process.

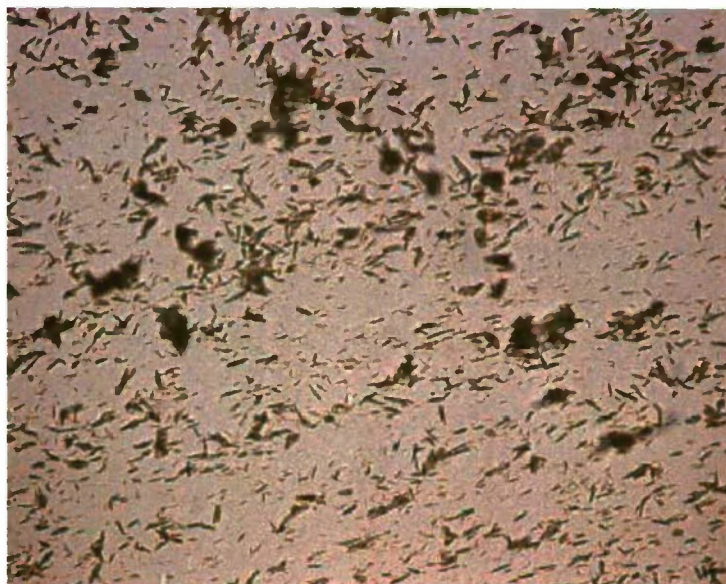


Figure 8

Optical microscope picture (500X) of NQ crystals obtained from spray drying of a NQ solution in water

Studies for Determination of Kinetics

Determination of Dissolved Nitroguanidine Concentration using Infrared Spectroscopy

The NQ absorbance spectra by IR radiation were taken in water solution. Figure 9 shows the absorbance values at different wavelengths and it appears that NQ absorbs IR light at around wave number 1281 cm^{-1} . Calibration of the absorbance as a function of different known NQ concentrations was done. Figure 10 shows results of the calibration.

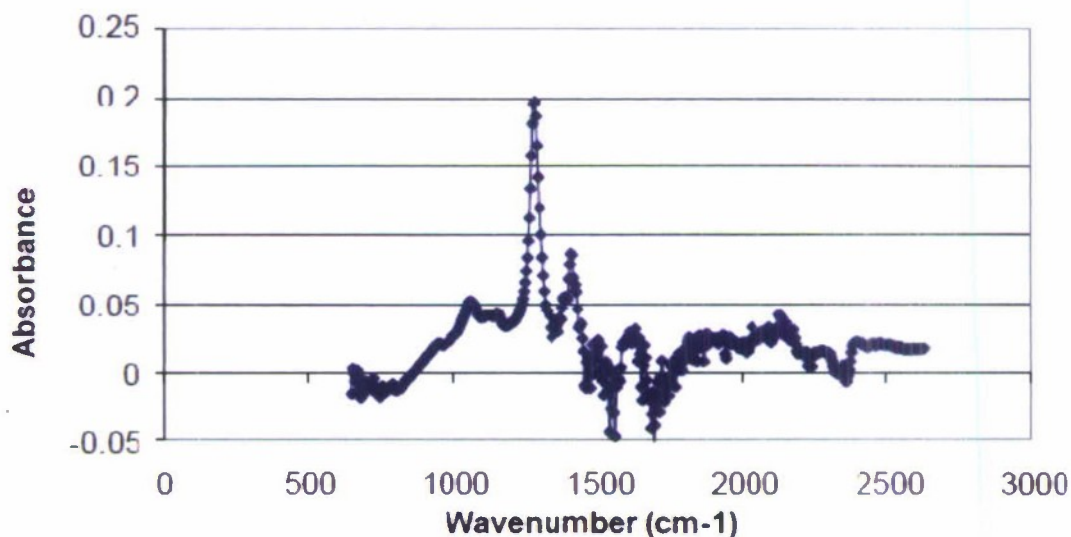


Figure 9
IR absorption of NQ solution in water

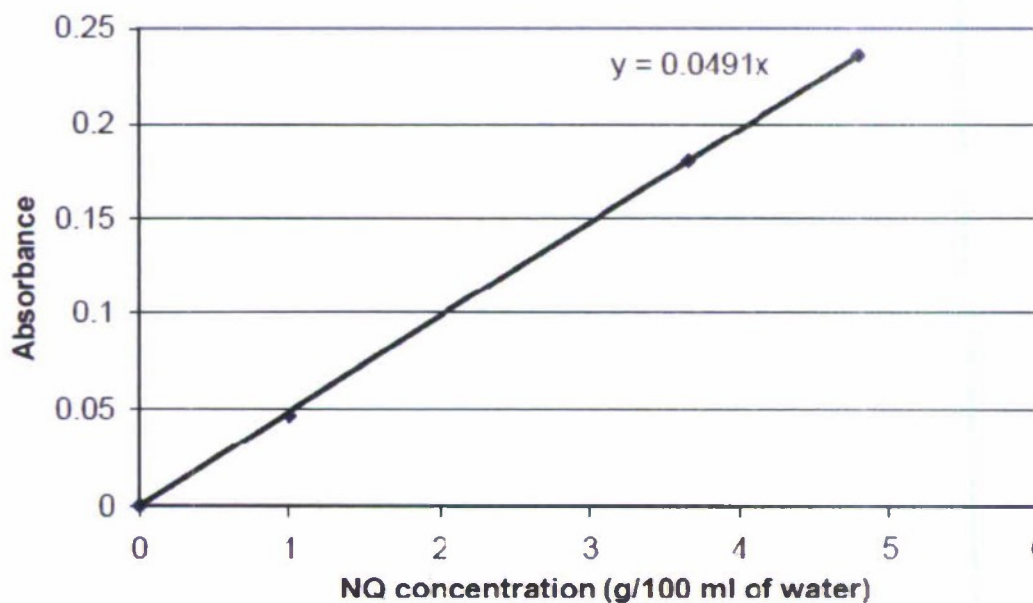


Figure 10
Calibration of absorbance as a function of known NQ concentration

Measurements of Nitroguanidine Solubility in Water

The solubility of NQ in water at different temperatures was determined as follows:

Saturated solution of NQ (containing both dissolved and undissolved solid NQ) was allowed to equilibrate at a known temperature. A known volume of clear supernatant solution was dried on a hot plate at 100°C and the weight of solid crystals was measured from which the solubility was calculated. The solubility values at different temperature levels were determined in similar ways. The solubility obtained at different temperatures follows:

Temperature (°C)	Solubility (g NQ/100 mL of water)
20.0	0.2880
34.8	0.5557
49.8	1.1941
64.6	2.0633

Based on the measured solubility values, the equation for solubility as a function of temperature was obtained (fig. 11). Solubility, thus obtained, can be expressed by the following equation:

$$\text{Solubility (g NQ/100 mL of water)} = 10^{(-1928.14/(T+273.14)+6.0286)}, \text{ T is in degrees Celsius}$$

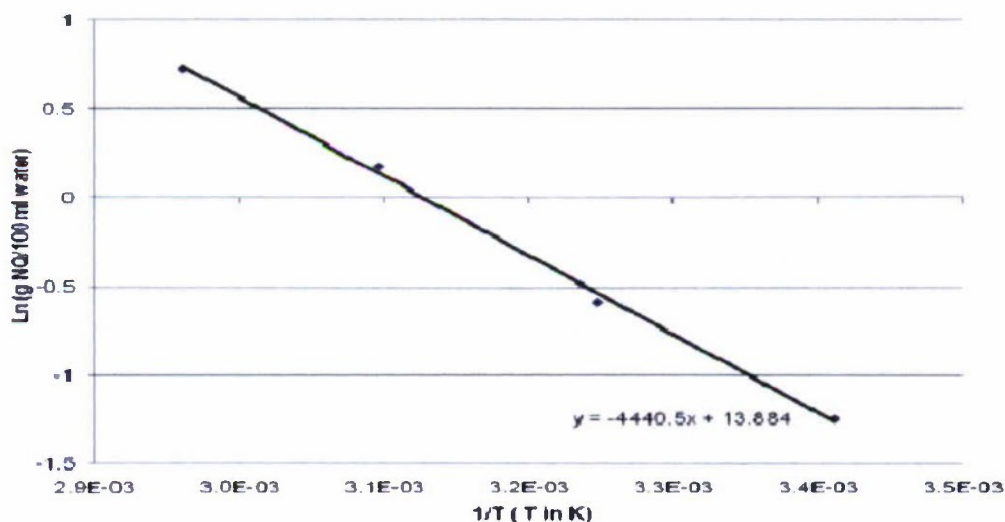


Figure 11
Measured NQ solubility as a function of temperature

Calculation of Supersaturation

Values of supersaturation at any time is taken as the difference between the actual dissolved NQ concentration measured from the IR spectroscopy and the solubility of NQ at the temperature corresponding at that time. Figure 12 shows a plot of dissolved NQ concentration at different temperatures corresponding to a cooling rate of 2.5°C/min. The supersaturation at any time can be calculated from the difference of actual concentration in the solution and the solubility corresponding to the temperature at that time.

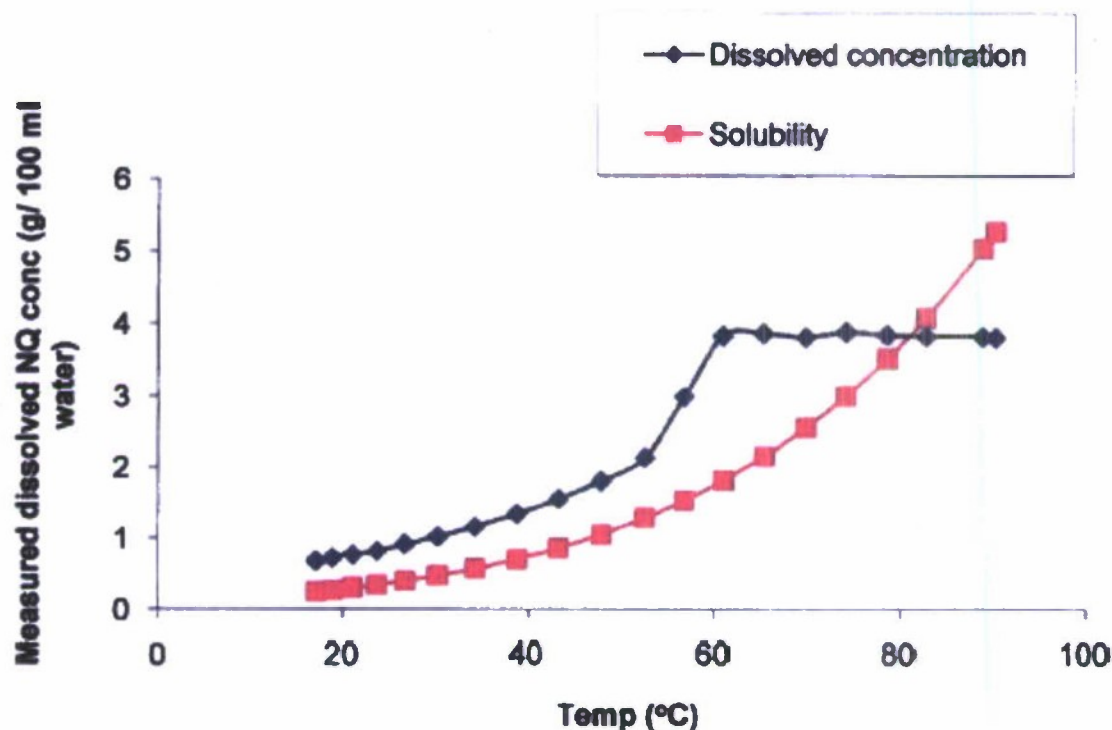


Figure 12
Measured concentration and solubility of NQ at a cooling rate of 2.5°C/min in water solution containing methylcellulose and PVA

Crystallization Kinetics

As seen in figure 12, an appreciable level of supersaturation exists during crystallization of NQ. The kinetics of the NQ crystallization was studied by adding NQ seeds to a supersaturated solution under isothermal condition. The change in supersaturation was continuously monitored by measuring the dissolved NQ concentration in the solution using the IR probe. The seeds were first prepared as follows:

Methylcellulose (360 mg) and 720 mg of partially hydrolyzed PVA were dissolved in 120 mL of deionized water by leaving the solution overnight. It was filtered to remove any undissolved impurities. The solution was first cooled in air then sonicated in a cold bath. The crystals were filtered and washed with acetone. Seeds of mean size of approximately 12 μm were obtained. A microscope picture of the seeds is shown in figure 13.

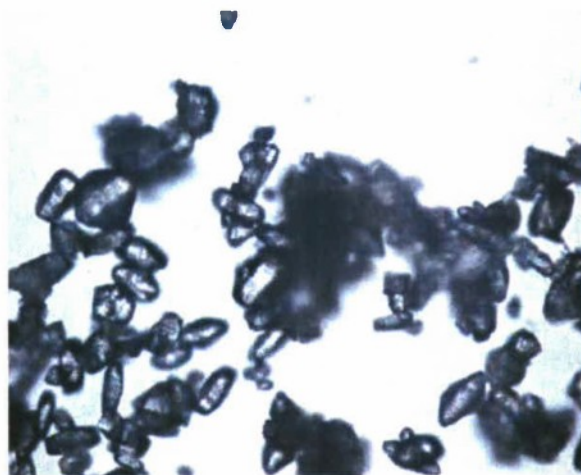


Figure 13
Microscope picture of seeds at 500x magnification

For making the desupersaturation kinetic runs, NQ in water along with additives were heated to a temperature so that all the solutes completely dissolved. The solution was then cooled gradually in the crystallizer vessel to a temperature so that 20 to 30% of supersaturation exists in the solution without any crystallization taking place and the temperature was kept constant. A known amount of dry seed was then added to this supersaturated solution at once. The crystallization started after adding the seeds and the concentration of the dissolved NQ was continuously measured using the IR probe. Figure 14 shows the change in the supersaturation level at 69°C with time and different amounts of seeds added. The rate of decrease in supersaturation with time is much slower in solution containing methylcellulose and PVA than in solution without any additives. This suggests that without methylcellulose and PVA, the growth of the crystals on one direction is very fast resulting in needle structured crystals, while methylcellulose and PVA slow the growth in that direction resulting in more uniform growth in all directions forming bulkier crystals.

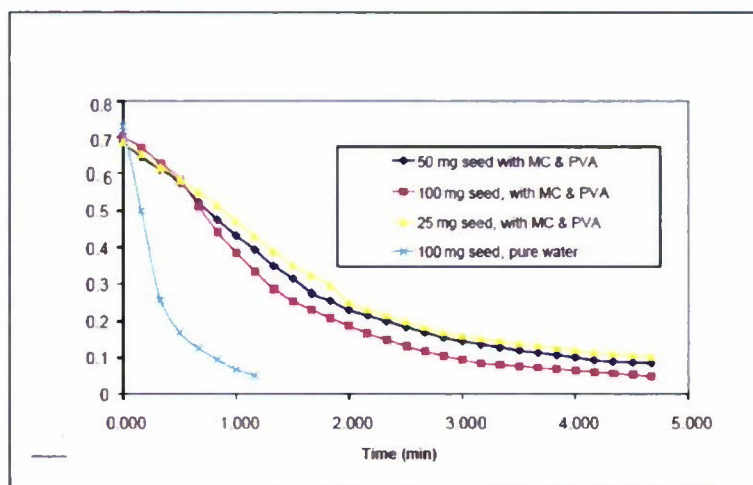


Figure 14
Experimental desupersaturation curves obtained at 69°C with different amounts of seeds in water solution with and without methyl cellulose and PVA

Optical microscope pictures of the crystals obtained from the solution at 69°C are shown in figure 15. It is clear from this picture that without the additives, the growth of the crystals in one direction is many times faster than the other directions resulting in needle shape.

Similar desupersaturation measurements were also taken at a temperature of 44°C in water solution with methylcellulose and PVA as additives using different amount of seeds.

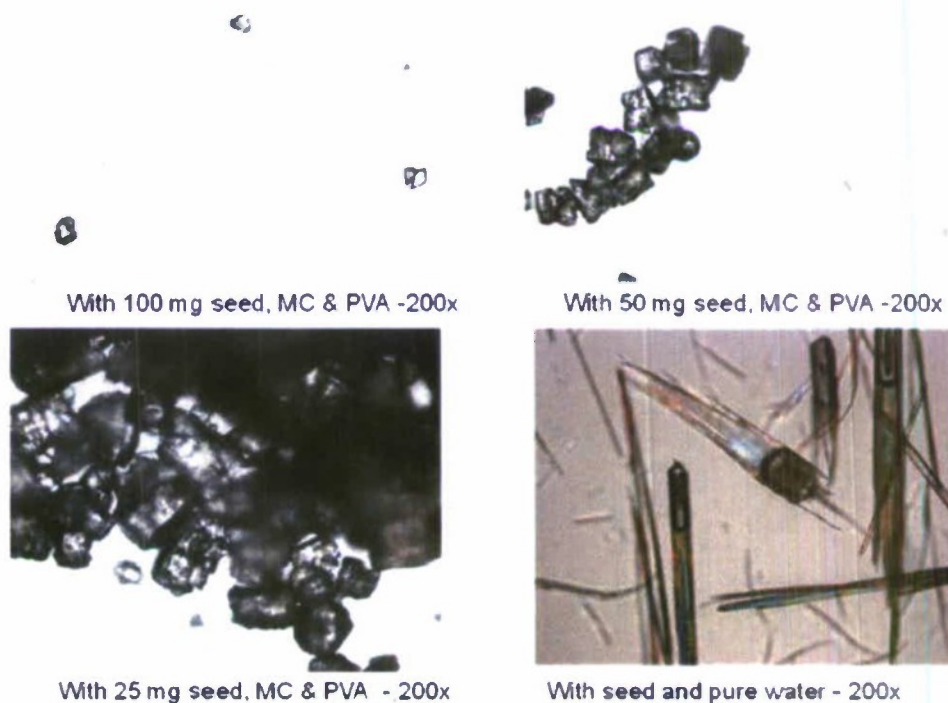


Figure 15
Optical microscope pictures of crystals obtained after desupersaturation

CONCLUSIONS

High bulk density nitroguanidine (NQ) was successfully produced by controlled cooling of a supersaturated solution of NQ in water containing methylcellulose and PVA, while many other methods studied in this work yielded only needle or rod shaped crystals. From the studies on crystallization kinetics from supersaturated solution by using seeds, it appears that without methylcellulose and PVA, the crystals grow very fast in one direction resulting in needle or rod shaped crystals, whereas, methylcellulose and PVA restrict growth in that direction resulting in more uniform growth in all directions, which give bulkier crystals.

RECOMMENDATIONS

A detailed kinetic model using the experimental data presented in this work should be investigated. In the model equation order of crystal growth, growth rate coefficient, and the dependency of growth rate coefficient on temperature should be evaluated.

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